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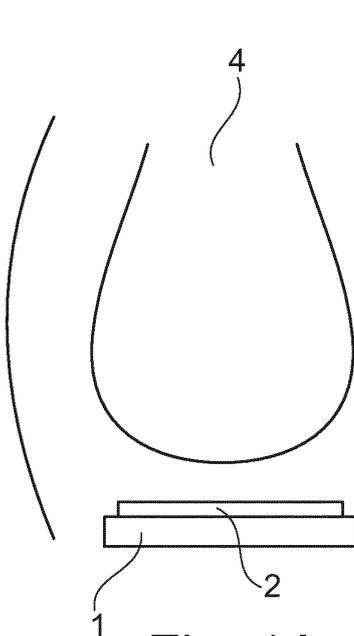
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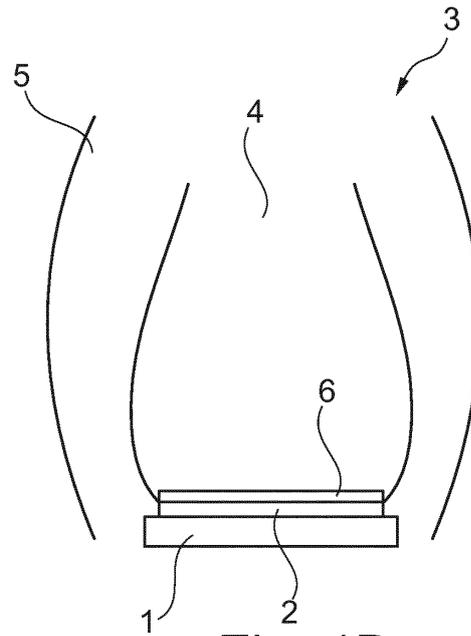
(54) **Method for depositing a target material onto a sensitive material**

(57) The invention relates to a method for depositing a target material onto a sensitive material, which method comprises the steps of:  
- providing a substrate with a sensitive material, like an emissive electroluminescent layer;  
- creating a vapor plume of target material by a physical vapor deposition method;  
- depositing a first layer of target material on the sensitive

material, while maintaining the maximum particle velocity of the deposited particles below a preset value; and  
- depositing a second layer of target material on the first layer of target material, while the maximum particle velocity of the deposited particles is above the preset value.  
The invention also relates to an intermediate product and to an organic light emitting diode.



**Fig. 1A**



**Fig. 1B**

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## Description

**[0001]** The invention relates to a method for depositing a target material onto a sensitive material.

**[0002]** Depositing methods, and in particular physical vapor deposition methods, use a plume of vapor with particles, which are bombarded onto a substrate material. This plume of vapor is generated by exciting a target material, such that particles are freed from the target material. Due to the excitement, the particles gain kinetic energy, which moves the particles to the substrate and which energy is used for the particles to adhere to the substrate or even penetrate the substrate material. Depending on the substrate material and the obtained kinetic energy, the particles will penetrate to a certain depth of the substrate material and/or damage the material due to the bombardment. In the field of organic light emitting diodes (OLEDs) efforts are made to provide transparent OLEDs. An OLED has typically a layered structure of a glass or transparent plastic layer, a first conducting layer, an emissive electroluminescent layer and a second conducting layer. By providing a voltage to the first and second conducting layer, the emissive electroluminescent layer is powered, such that it will emit light.

**[0003]** A transparent emissive electroluminescent layer is known, as well as transparent conducting layers. Typically an indium tin oxide layer is used for a transparent conducting layer, which is arranged on a substrate with a physical vapor deposition method. However, if a known physical vapor deposition method is used to deposit indium tin oxide, or a similar transparent conducting oxide, to the transparent emissive electroluminescent layer, the impact of the particles damages the emissive electroluminescent layer to the extent, that it no longer emits light when being powered, or its efficiency is strongly reduced due to a leakage current or short circuiting.

**[0004]** It is known to use a silver deposition on the emissive electroluminescent layer. Silver has the advantage that it can be deposited under such conditions, that it will not damage the emissive electroluminescent layer. However, the transparency of a silver layer is restricted. Typically, an OLED with a silver layer as one of the conductive layers can have a transparency of up to 40%.

**[0005]** Another disadvantage of the known methods, in particular laser deposition methods, is that they use ultraviolet light. Ultraviolet light damages the materials, which are typically used for OLED production. UV light in combination with the bombardment of particles is typically damaging for organic materials used for OLED production.

**[0006]** A possibility would be to arrange a protective layer of another material, which blocks ultraviolet light. However, such layers are often not transparent and in the case when an electrically conducting layer is to be arranged, the protective layer will isolate the electrically conducting layer from the emissive electroluminescent layer.

**[0007]** It is therefore an object of the invention to pro-

vide a method, in which the above mentioned disadvantages are reduced or even prevented.

**[0008]** This object is achieved with a method according to the preamble, which method comprises the steps of:

- providing a substrate with a sensitive material, like an emissive electroluminescent layer;
- creating a vapor plume of target material by a physical vapor deposition method;
- depositing a first layer of target material on the sensitive material, while maintaining the maximum particle velocity of the deposited particles below a preset value; and
- depositing a second layer of target material on the first layer of target material, while the maximum particle velocity of the deposited particles is above the preset value.

**[0009]** With the method according to the invention, a first layer of target material is arranged on the sensitive material without destroying the material. This is achieved by ensuring that the maximum particle velocity is maintained below a preset value. When the particle velocity, and thus the kinetic energy, of the particles is below a preset value, the particles will attach to the sensitive material, but will not penetrate and/or damage the sensitive material, which could negatively affect the sensitive material.

**[0010]** In case an UV laser is used for creating the vapor plume, the first layer could also provide an UV protection for the sensitive material, such that a higher UV intensity can be used during deposition of the second layer. In an embodiment of the invention the distance between the target material and the substrate is increased during depositing the first layer and said distance is decreased during depositing the second layer. This results in a lower maximum particle velocity on impact of the particles on the substrate and also a lower UV intensity on the substrate when the first layer is deposited.

**[0011]** Then the second layer is deposited on the first layer. The already deposited layer provides a protective layer for the sensitive material, so the target material particles for the second layer can have a higher velocity during depositing than the target material particles used for the first layer.

**[0012]** With the method according to the invention, it is, because of the first layer, thus possible to deposit the target material in a conventional way on a sensitive material, which would otherwise damage the sensitive material.

**[0013]** The preset value will have to be determined by experiment as the preset value will at least depend on the material of the target material, the physical vapor deposition method, the chosen deposition parameters and the sensitive material.

**[0014]** In a preferred embodiment of the method according to the invention the first layer is deposited while using a first pressure regime, the second layer is depos-

ited while using a second pressure regime and wherein the second pressure is lower than the first pressure.

**[0015]** With a physical depositing method a near vacuum environment is created in which the depositing is performed. By controlling the vacuum or the pressure in this environment, the impact velocity of the particles can be controlled. When a higher pressure regime is used, the particles of the target material in the vapor plume are slowed down more, such that the impact on the substrate is less violent and the sensitive material is no longer affected. With a higher pressure regime, the particles have a 'soft landing' on the sensitive material.

**[0016]** As soon as the first layer is deposited with the target material, the pressure regime can be lowered, such that the particles can keep their speed and impact with full energy on the first layer, without damaging the underlying sensitive material.

**[0017]** Although it would be most common to deposit the first and second layer with the same material, it will also be possible to change the target material before depositing the second layer. By using two different target materials, specific properties can be achieved for the layer deposited on the sensitive material.

**[0018]** In a further preferred embodiment of the method according to the invention the vapor plume is moved over the surface of the sensitive material and the vapor plume is controlled such, that the maximum velocity of the particles in the core of the plume is above the preset value and the maximum velocity of the particles around the core is below the preset value.

**[0019]** When a vapor plume is generated by exciting a target material with for example a laser beam, the vapor plume will have a core with a high concentration of particles having a high velocity. This core is surrounded with an envelope with a lower concentration of particles. The particles in the envelope will have a lower velocity.

**[0020]** By moving the vapor plume over the surface of the sensitive material, the envelope with lower concentration of particles will deposit first on the sensitive material. This provides the sensitive material with the first layer of target material along the path of the plume. While the plume moves further, the core will pass over the material already deposited by the envelope of the plume. The particles within the core of the plume will then deposit the second layer of target material.

**[0021]** Preferably, the movement of the vapor plume starts outside of the surface of the sensitive material. This ensures, that both the first layer and second layer of target material extend to the full surface of the sensitive material.

**[0022]** When the vapor plume is moved over the surface of the sensitive material it is necessary that the maximum velocity of the particles in the core of the plume is above the preset value and the maximum velocity of the particles around the core is below the preset value. Due to the way a vapor plume is generated, there is already a difference in particle velocity of the particles in the core and the particles enveloping the core. Choosing a suitable

pressure regime, will ensure, that the maximum particle velocity of the particles in the envelope is below the preset value, while the maximum velocity in the core is higher.

5 **[0023]** In yet another embodiment of the method according to the invention the physical vapor deposition method is a pulsed laser deposition.

**[0024]** In a further embodiment of the method according to the invention, the combined first and second layer is a transparent conducting oxide, in particular indium tin oxide.

**[0025]** A transparent conducting oxide is a typical material, which could not be arranged on a sensitive material, like an emissive electroluminescent layer, without the method according to the invention.

10 **[0026]** The invention also relates to an intermediate product manufactured with the method according to the invention, wherein the product comprises:

- 20 - a substrate with a sensitive material, like an emissive electroluminescent layer;
- a first layer of target material deposited on the sensitive material, wherein the deposited particles have marginally penetrated and/or damaged the sensitive material.

**[0027]** With the intermediate product of the invention, a first layer of target material is arranged on the substrate with a sensitive material. The deposited particles have marginally penetrated the sensitive material, such that the sensitive material is not affected. The particles are arranged on the sensitive material and have not, or only slightly, penetrated the sensitive material.

30 **[0028]** The invention also relates to an organic light emitting diode comprising:

- a substrate layer;
- a first electric conducting layer arranged on the substrate layer;
- 40 - an emissive electroluminescent layer arranged on the first electric conducting layer; and
- a second electric conducting layer arranged on the emissive electroluminescent layer;

45 wherein the second electric conducting layer is arranged using the method according to the invention.

**[0029]** These and other features of the invention will be elucidated in conjunction with the accompanying drawings.

50 **[0030]** Figure 1A and 1B show two steps of a first embodiment according to the invention.

**[0031]** Figure 2 shows a second embodiment of the method according to the invention.

**[0032]** Figure 3 shows a cross sectional view of an embodiment of the organic light emitting diode according to the invention.

55 **[0033]** Figure 1A shows a first step of a first embodiment of the method according to the invention. A sub-

strate 1 is provided with a layer of sensitive material 2. A vapor plume 3 with particles of a target material is generated with a physical vapor deposition method, such as a pulsed laser deposition method. This vapor plume 3 has a core 4 and an envelope 5.

**[0034]** By controlling the pressure regime in which the vapor plume 3 is generated, the reach of the plume 3 and the impact of the particles within the plume 3 can be controlled. In the step shown in figure 1A, the pressure is relative high, such that the kinetic energy of the particles within the plume 3 is reduced and the particles have a 'soft landing' on the surface of the sensitive material and form a first layer of target material 6.

**[0035]** In the step shown in figure 1B, the pressure is reduced, such that the particles within the plume 3 keep their kinetic energy and are deposited on top of the first layer of target material 6 in the conventional way to form the second layer of target material. Because the first layer 6 is already arranged on top of the sensitive material 2, protecting this layer 2 and enabling conventional deposition of a second layer.

**[0036]** Figure 2 shows a second embodiment of the method according to the invention. A substrate 10 is provided with a layer 11 of a sensitive material. Furthermore, a vapor plume 12 is generated. This vapor plume 12 has a core 13 with particles having a relative high velocity, and an envelope 14 around the core 13 with particles with a relatively low velocity.

**[0037]** The plume 12 is moved over the surface of the sensitive material 11. The envelope 14 deposits first a first layer 15 of target material of the sensitive material 11. The trailing core 13 then deposits a second layer 16 on the already deposited first layer 15. As the first layer 15 and second layer 16 are deposited with the same target material particles, a virtually homogeneous layer of target material on top of the sensitive material 11 is created.

**[0038]** Figure 3 shows an embodiment 20 of an organic light emitting diode (OLED). This OLED 20 has a substrate layer 21, like a glass layer. A first conductive layer 22 is deposited with a conventional physical vapor deposition method on this substrate layer 21. Then an emissive electroluminescent layer 23 is provided on top of the conductive layer 22.

**[0039]** With the method according to the invention a second conductive layer 24, 25 is arranged on top of the sensitive, emissive electroluminescent layer 23. The first layer 24 of transparent conductive material is first deposited, after which the second layer 25 of transparent conductive material is deposited. Because both layers 24, 25 are subsequently deposited, a homogeneous layer is provided on the emissive electroluminescent layer 23.

**[0040]** When a voltage is applied to the two conductive layers 22 and 24, 25 the emissive electroluminescent layer 23 will emit light. As both conductive layers can be made transparent using for example indium tin oxide, a fully transparent OLED is obtained.

## Claims

1. Method for depositing a target material onto a sensitive material, which method comprises the steps of:
  - providing a substrate with a sensitive material, like an emissive electroluminescent layer;
  - creating a vapor plume of target material by a physical vapor deposition method;
  - depositing a first layer of target material on the sensitive material, while maintaining the maximum particle velocity of the deposited particles below a preset value; and
  - depositing a second layer of target material on the first layer of target material, while the maximum particle velocity of the deposited particles is above the preset value.
2. Method according to claim 1, wherein the first layer is deposited while using a first pressure regime, the second layer is deposited while using a second pressure regime and wherein the second pressure is lower than the first pressure.
3. Method according to claim 1, wherein the vapor plume is moved over the surface of the sensitive material and the vapor plume is controlled such, that the maximum velocity of the particles in the core of the plume is above the preset value and the maximum velocity of the particles around the core is below the preset value.
4. Method according to claim 3, wherein the movement of the vapor plume starts outside of the surface of the sensitive material.
5. Method according to claim 1, wherein the distance between the target material and the substrate is increased during depositing the first layer and said distance is decreased during depositing the second layer.
6. Method according to any of the preceding claims, wherein the physical vapor deposition method is a pulsed laser deposition.
7. Method according to any of the preceding claims, wherein the combined first and second layer is a transparent conducting oxide, in particular indium tin oxide.
8. Intermediate product manufactured with the method according to any of the preceding claims, wherein the product comprises:
  - a substrate with a sensitive material, like an emissive electroluminescent layer;
  - a first layer of target material deposited on the

sensitive material, wherein the deposited particles have marginally penetrated the sensitive material.

9. Organic light emitting diode comprising: 5
- a substrate;
  - a first electric conducting layer arranged on the substrate;
  - an emissive electroluminescent layer arranged on the first electric conducting layer; and 10
  - a second electric conducting layer arranged on the emissive electroluminescent layer;
- characterized in that** the second electric conducting layer is arranged using the method according to any of the claims 1 - 7. 15

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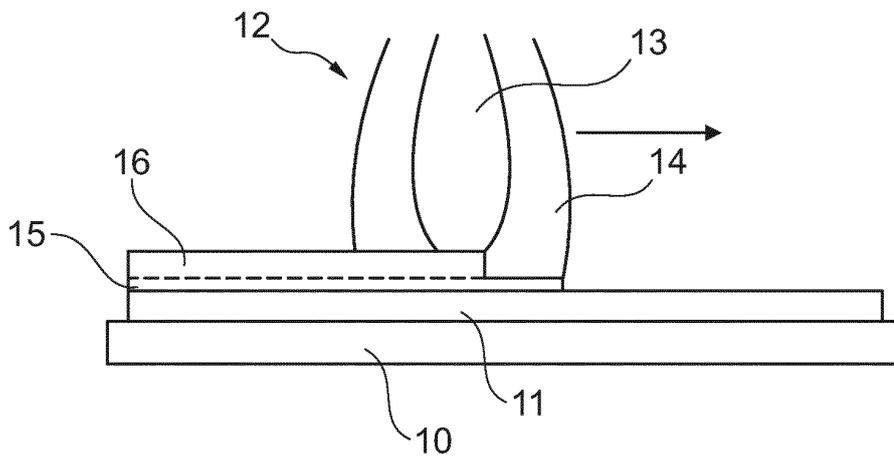
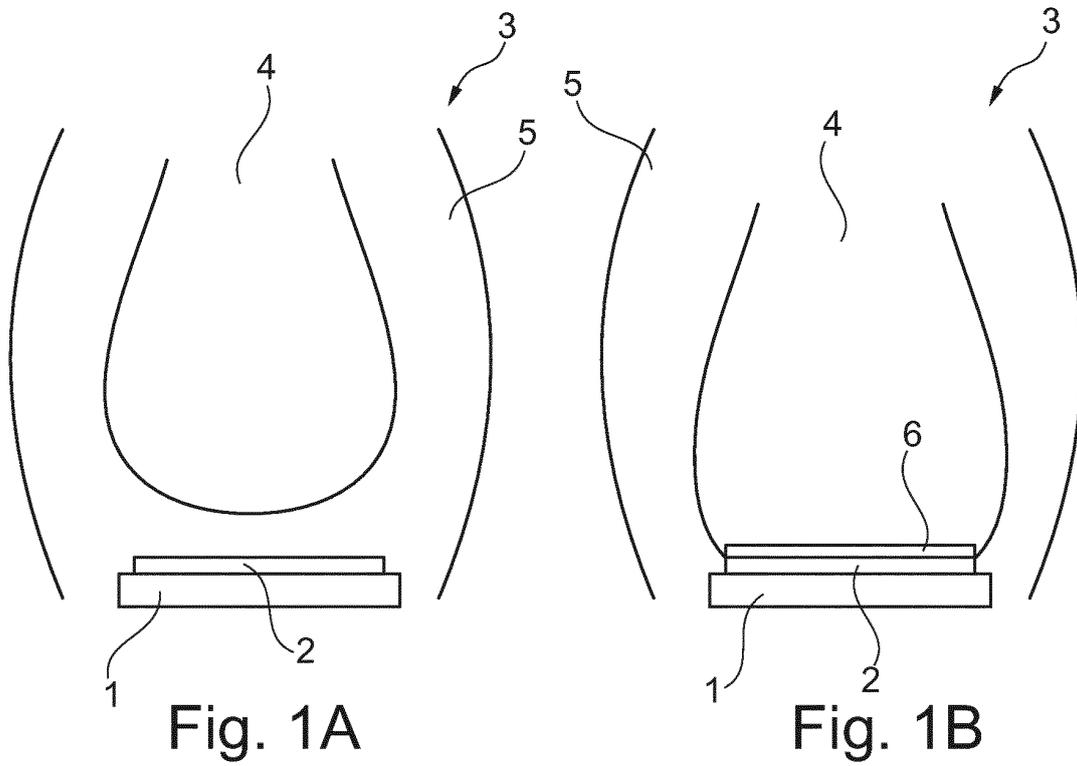


Fig. 2

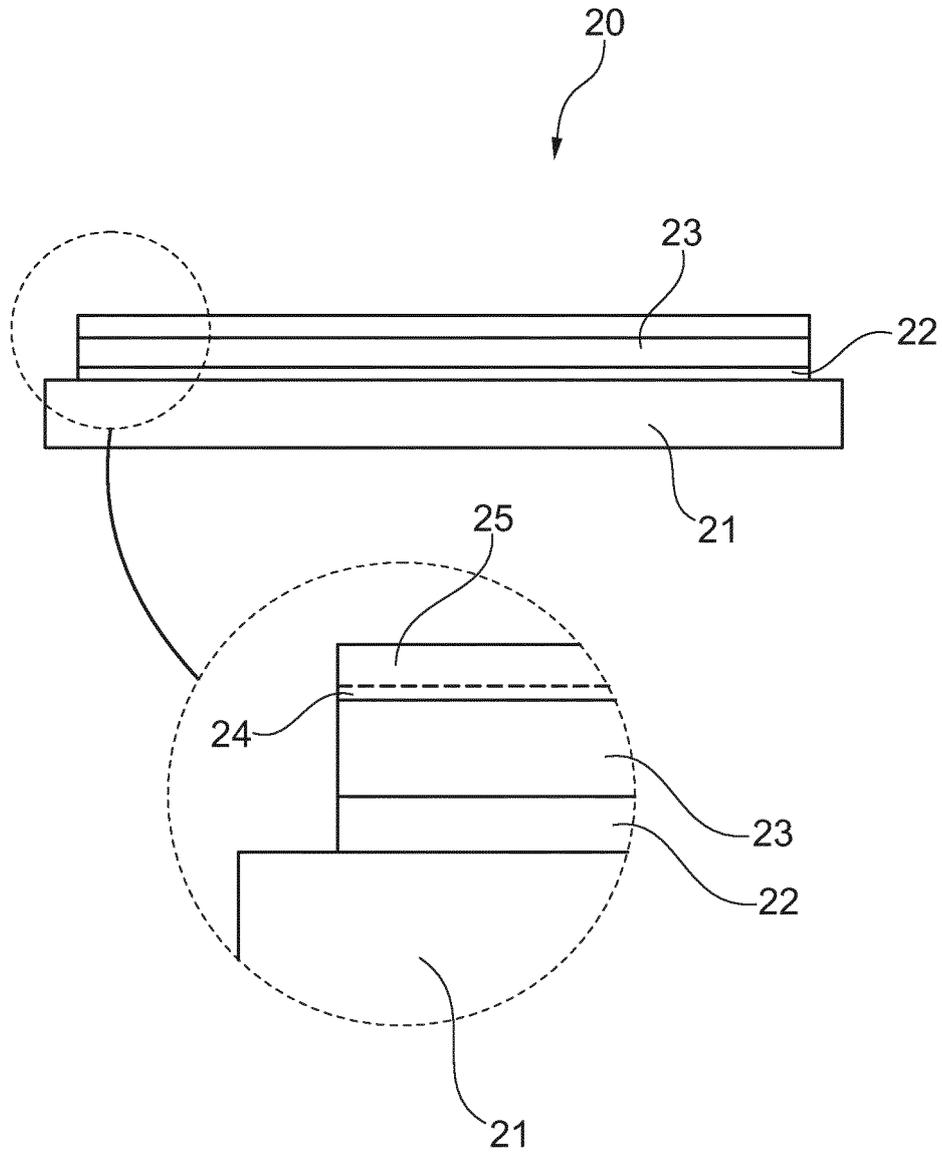


Fig. 3



EUROPEAN SEARCH REPORT

Application Number  
EP 12 18 8835

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A	----- -/--	1,2,6,7	
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 31 May 2013	Examiner Brisson, Olivier
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	

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EPC FORM 1503 03.82 (P/4C01)



EUROPEAN SEARCH REPORT

Application Number  
EP 12 18 8835

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The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 31 May 2013	Examiner Brisson, Olivier
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	

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EPO FORM 1503 03.02 (P/4C01)



EUROPEAN SEARCH REPORT

Application Number  
EP 12 18 8835

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	MEYER J ET AL: "Indium-free transparent organic light emitting diodes with Al doped ZnO electrodes grown by atomic layer and pulsed laser deposition", APPLIED PHYSICS LETTERS, AIP, AMERICAN INSTITUTE OF PHYSICS, MELVILLE, NY, US, vol. 93, no. 7, 22 August 2008 (2008-08-22), pages 73308-73308, XP012113590, ISSN: 0003-6951, DOI: 10.1063/1.2975176 * the whole document *	8	TECHNICAL FIELDS SEARCHED (IPC)
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The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 31 May 2013	Examiner Brisson, Olivier
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	

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EPO FORM 1503 03 82 (P04G01)



EUROPEAN SEARCH REPORT

Application Number  
EP 12 18 8835

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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			TECHNICAL FIELDS SEARCHED (IPC)
The present search report has been drawn up for all claims			
Place of search <b>Munich</b>		Date of completion of the search <b>31 May 2013</b>	Examiner <b>Brisson, Olivier</b>
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone                      Y : particularly relevant if combined with another document of the same category                      A : technological background                      O : non-written disclosure                      P : intermediate document</p> <p>T : theory or principle underlying the invention                      E : earlier patent document, but published on, or after the filing date                      D : document cited in the application                      L : document cited for other reasons                      .....                      &amp; : member of the same patent family, corresponding document</p>			

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EPO FORM 1503 03.82 (P04C01)



Application Number

EP 12 18 8835

**CLAIMS INCURRING FEES**

The present European patent application comprised at the time of filing claims for which payment was due.

- Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due and for those claims for which claims fees have been paid, namely claim(s):
- No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due.

**LACK OF UNITY OF INVENTION**

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

- All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.
- As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.
- Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:
- None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:
- The present supplementary European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims (Rule 164 (1) EPC).



**LACK OF UNITY OF INVENTION  
SHEET B**

Application Number  
EP 12 18 8835

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. claims: 2(completely); 1, 6, 7, 9(partially)

Method for depositing a target material onto a sensitive material, which method comprises the steps of:- providing a substrate with a sensitive material, like an emissive electroluminescent layer;- creating a vapor plume of target material by a physical vapor deposition method;- depositing a first layer of target material on the sensitive material, while maintaining the maximum particle velocity of the deposited particles below a preset value; and- depositing a second layer of target material on the first layer of target material, while the maximum particle velocity of the deposited particles is above the preset value, wherein the first layer is deposited while using a first pressure regime, the second layer is deposited while using a second pressure regime and wherein the second pressure is lower than the first pressure. An organic light emitting diode, which production involves the above method.

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2. claims: 3, 4(completely); 1, 6, 7, 9(partially)

Method for depositing a target material onto a sensitive material, which method comprises the steps of:- providing a substrate with a sensitive material, like an emissive electroluminescent layer;- creating a vapor plume of target material by a physical vapor deposition method;- depositing a first layer of target material on the sensitive material, while maintaining the maximum particle velocity of the deposited particles below a preset value; and- depositing a second layer of target material on the first layer of target material, while the maximum particle velocity of the deposited particles is above the preset value and wherein the vapor plume is moved over the surface of the sensitive material and the vapor plume is controlled such, that the maximum velocity of the particles in the core of the plume is above the preset value and the maximum velocity of the particles around the core is below the preset value. An organic light emitting diode, which production involves the above method.

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3. claims: 5(completely); 1, 6, 7, 9(partially)

Method for depositing a target material onto a sensitive material, which method comprises the steps of:- providing a substrate with a sensitive material, like an emissive electroluminescent layer;- creating a vapor plume of target material by a physical vapor deposition method;- depositing a first layer of target material on the sensitive material, while maintaining the maximum particle velocity of the



**LACK OF UNITY OF INVENTION  
SHEET B**

Application Number  
EP 12 18 8835

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

deposited particles below a preset value; and- depositing a second layer of target material on the first layer of target material, while the maximum particle velocity of the deposited particles is above the preset value and wherein the distance between the target material and the substrate is increased during depositing the first layer and said distance is decreased during depositing the second layer. An organic light emitting diode, which production involves the above method.

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4. claims: 1, 6, 7(all partially)

Method for depositing a target material onto a sensitive material, which method comprises the steps of:- providing a substrate with a sensitive material, like an emissive electroluminescent layer;- creating a vapor plume of target material by a physical vapor deposition method;- depositing a first layer of target material on the sensitive material, while maintaining the maximum particle velocity of the deposited particles below a preset value; and- depositing a second layer of target material on the first layer of target material, while the maximum particle velocity of the deposited particles is above the preset value and wherein the physical vapor deposition method is a pulsed laser deposition. An organic light emitting diode, which production involves the above method.

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5. claims: 1, 7(all partially)

Method for depositing a target material onto a sensitive material, which method comprises the steps of:- providing a substrate with a sensitive material, like an emissive electroluminescent layer;- creating a vapor plume of target material by a physical vapor deposition method;- depositing a first layer of target material on the sensitive material, while maintaining the maximum particle velocity of the deposited particles below a preset value; and- depositing a second layer of target material on the first layer of target material, while the maximum particle velocity of the deposited particles is above the preset value and wherein the combined first and second layer is a transparent conducting oxide. An organic light emitting diode, which production involves the above method.

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6. claim: 8

A product comprising:- a substrate with a sensitive material, like an emissive electroluminescent layer;- a



**LACK OF UNITY OF INVENTION  
SHEET B**

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The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

first layer of target material deposited on the sensitive material, wherein the deposited particles have marginally penetrated the sensitive material.

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**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 12 18 8835

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

31-05-2013

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